Olivine/liquid partitioning, heats of fusion, and the illusion of linearity

J.H. JONES

KR, NASA/JSC, Houston, TX 77058
(john.h.jones@nasa.gov)

Several elements, particularly first-row transition elements, show very good, linear D (i) vs. D (Mg) correlations for olivine/liquid [1]. For some elements this relationship can be straightforwardly explained. Using FeO as an example, a thermodynamic analysis of D (Fe) vs. D (Mg) shows that the slope of the data trend should have the form:

$$\partial D\ (\mathrm{Fe})/\partial D\ (\mathrm{Mg}) = K_D\ (\mathrm{Fe/Mg}) * \Delta H_{\mathrm{Fa}}/\Delta H_{\mathrm{Fo}} \quad (1)$$

where K_D (Fe/Mg) is the Fe-Mg exchange coefficient and ΔH is the heat of fusion of fayalite or forsterite. Because the heats of fusion of fayalite and forsterite are subequal, equation (1) predicts that the slope of the D vs. D line will be nearly constant and have a value that is essentially that of K_D. For D (Fe) and D (Mn) vs. D (Mg), this prediction is shown to be true. A further prediction is that the D vs. D line will have a y-intercept very near the origin (i. e., K_D is nearly constant), and this prediction is also fulfilled.

D (Ni) also is linear with D (Mg). But in this case, the data array does not pass close to the origin and therefore, K_D cannot be constant. Further, the heat of fusion of Ni-olivine is nearly twice that of forsterite, so the heat of fusion term in eq. (1) can no longer be ignored.

An approximate solution to these contrarian observations may be found by noting empirically that

$$D\ (\mathrm{Ni}) = a\ D\ (\mathrm{Mg}) + b \quad (2)$$

and that

$$K_D\ (\mathrm{Ni/Mg}) = a + b/D\ (\mathrm{Mg}) \quad (3)$$

Substituting eq. (3) into eq. (1) and integrating yields:

$$D\ (\mathrm{Ni}) =[a\ (D\ (\mathrm{Mg})\ -1) + b\ \ln D\ (\mathrm{Mg})]\ \Delta H_{\mathrm{Ni\text{-}ol}}/\Delta H_{\mathrm{Fo}} \quad (4)$$

It is found that a function of this form (i) is nearly linear over a large range of D (Ni) and (ii) fits the combined data of Longhi *et al.* [2] and Leeman and Lindstrom [3] very well. However, this functionality makes the suggestion of [2] less probable — i. e., that Ni may become incompatible in lunar olivines at high temperatures.

[1] Jones (1984) *Cont. Min. Pet.* **88**, 126–132. [2] Longhi *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 784–798. [3] Leeman & Lindstrom (1978) *Geochim. Cosmochim. Acta* **42**, 801–816.

Non-reductive dissolution of iron oxides by *Shewanella oneidensis* during dissimilatory Fe(III) reduction

M.E. JONES[1], C.M. FENNESSEY[2], T.J. DICHRISTINA[2] AND M. TAILLEFERT[1]*

[1]School of Earth and Atmospheric Sciences, Georgia Institue of Technology, Atlanta, GA 30332 USA
(*correspondence: mtaillef@eas.gatech.edu)
[2]School of Biology, Georgia Institue of Technlogy, Atlanta, GA 30332 USA

Dissimilatory iron reducing bacteria impact a variety of geochemical processes from iron and carbon cycling to the bioremediation of contaminated systems, yet the mechanism of anaerobic respiration of Fe (III) remains unknown. Proposed electron transfer pathways include the direct contact between the reductase and Fe (III) and the use of electron shuttling components or bacterial nanowires. Recently, *Shewanella putrefaciens* was shown to produce organic complexes of Fe (III) as intermediates during anaerobic Fe (III) respiration at rates that correlate with bacterial cell density and the number of available reactive surface sites.

In this study, the solubilization of Fe (III) oxides by endogenous organic ligands is demonstrated for the first time with *S. oneidensis* strain MR-1. Soluble organic-Fe (III) complexes are produced during anaerobic Fe (III) oxide respiration but not when alternate electron acceptors with reduction potentials greater than +0.15 volts are simultaneously provided, suggesting a redox threshold must be met prior to the onset of organic ligand synthesis. A novel Microelectrode Screening Array (MESA) was developed to identify four random mutants of *S. oneidensis* with impaired soluble organic-Fe (III) production (Sol mutants). Reduction rates of Fe (III) by the Sol mutants and the wild-type strain are proportional to the rates of soluble organic-Fe (III) production, suggesting again that these complexes are intermediates in the reduction of Fe (III) oxides. Experiments with known mutants of *S. oneidensis* reveal that the type-II secretion system and MtrB, a β-barrel protein embedded in the outer membrane, are involved in organic ligand production while c-type cytochromes peripherally attached to the cell surface are not essential to the solubilization process.

Overall, these studies indicate that endogenous organic ligands of *S. oneidensis* play a previously underestimated role in the reduction of Fe (III) by providing a rapidly reducible Fe (III) substrate for outer membranes reductases or a soluble substrate that can be transported within the cell for reduction by internal components of the electron transport chain.